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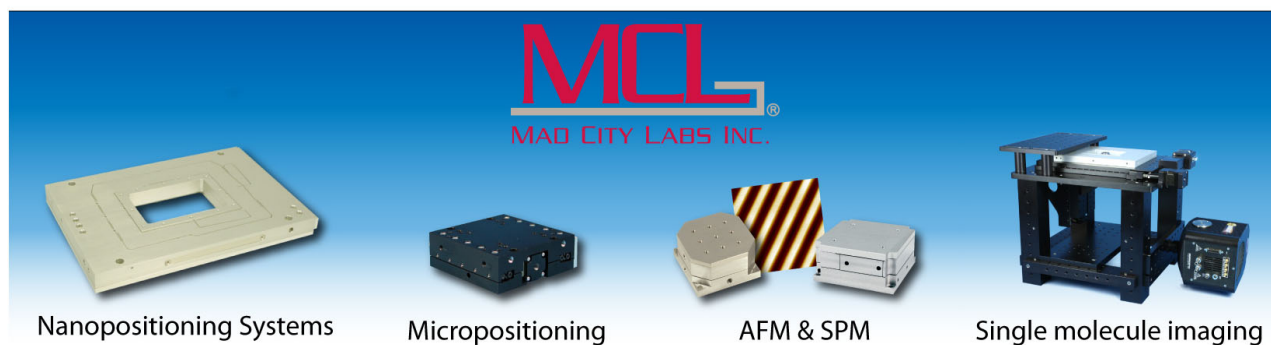
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High accuracy calibration of a dynamic vapor sorption instrument and determination of the equilibrium humidities using single salts

Inge Rörig-Dalgaard^{1,a)} and Staffan Svensson^{1,2}

¹Department of Civil Engineering, Technical University of Denmark, Kongens Lyngby, Denmark

²School of Engineering, University of Borås, Borås, Sweden

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We present a procedure for accurately calibrating a dynamic vapor sorption (DVS) instrument using single salts. The procedure accounts for and tailors distinct calibration tests according to the fundamental properties of each salt. Especially relevant properties influencing the calibration are the heat of solution, heat of condensation, and the kinetics connected to the salt phase transition, as these influence the microclimate surrounding the salts during calibration. All these issues were dealt with to obtain precise calibration results. The DVS instrument comprises two control modes to generate and measure the relative humidity (RH). Both control modes were separately examined and combined to overcome the shortcomings of each of the two control modes and thereby obtain the most accurate results. Repeated calibration testing with the single salts (LiCl, MgCl₂, Mg(NO₃)₂, NaCl, and KNO₃) enables five discrete sorption isotherm measurements within the range of 11%–93%RH. The equilibrium RH of the solution for LiCl, MgCl₂, Mg(NO₃)₂, NaCl, and KNO₃ was determined with a standard deviation of 0.06%–0.15% (0.45% for KNO₃) RH. By comparing the measured calibration values with the well-known equilibrium RH of each salt solution, the presented method's results are both accurate with significant agreement and precise with small variation. *Published by AIP Publishing*. [<http://dx.doi.org/10.1063/1.4949513>]

I. INTRODUCTION

A material's equilibrium moisture state relative to the surrounding climate is of utmost importance to its physical, chemical, biological, and mechanical performance. To obtain a material's hygroscopic behavior, the specimen should be accurately weighed under equilibrium moisture conditions in a known equilibrium moisture conditions at a known temperature. Additionally, the mass–climate relation must be determined with an acceptable level of uncertainty. Water vapor pressure (humidity) is a delicate climate parameter and the equilibrium relative humidity (RH) of a salt solution is essential for testing and calibrating hygrometers and for controlling humidity in closed spaces.¹ Saturated aqueous solutions of salts react to changes of the surrounding RH, so these solutions can be used for calibration purposes in an open system. In an open system, an imposed water vapor pressure leads to changes in the moisture content of a given material, whereas, in a closed system, the salt solutions control the climate. When studying a materials' equilibrium condition, an open system—where a known vapor pressure controls the process, is, therefore, a requirement.

The equilibrium RH of a solution is a physical property for which the rate of evaporation of water molecules from the solution is the same as the rate of condensation into the solution. Vapor will condense into a solution in an environment with a humidity above the equilibrium RH of the solution and evaporate in an environment, a humidity below the equilibrium

RH of the solution. Different saturated solutions have different specific equilibrium RH and saturated solutions of pure salts have a very precise equilibrium RH for any given temperature. Therefore, salts are useful for calibrating equipment requiring humidity precision.

A new method for validating the RH generated in sorption balances was reported for salt solutions with an equilibrium RH of 11%–75% RH (i.e., LiCl, MgCl₂, Mg(NO₃)₂, and NaCl).^{2,3} This validation was based on the rate of sample mass loss, which was proportional to the vapor pressure difference between the sample surface and the gas stream. To determine the equilibrium RH of the salt solution, Wadsö *et al.*² used quasi-randomly chosen constant RH levels, alternating between those above and below the equilibrium RH of the solution of each salt, and assumed that the rate of mass change was constant. The equilibrium RH levels found were based on the vapor pressure generated through the mass flow controllers of the dynamic vapor sorption (DVS) instrument. The mass transfer Biot numbers of the salts were determined to check whether internal gradients could be neglected. The shortcoming of Wadsö *et al.*, however, is not to include the effect of the salt phase transition on the surrounding microclimate as temperature change (dT) and RH change (dRH) while changing the moisture content (dm) through the imposed relative humidity of the gas stream, when validating the method with the sorption balance. The temperature change can be caused by heat of condensation and heat of solution. A temperature change alters the water activity in the solution through crystallization or dissolution of the salt resulting in non-accurate calibration results. Therefore, the present challenge is to interpret correctly how under these circumstances the imposed water vapor pressure can

^{a)}Author to whom correspondence should be addressed. Electronic mail: ird@byg.dtu.dk

be desirably adjusted or, respectively, calibrated under non-equilibrium experimental conditions aiming to ensure that the imposed gas stream has the desired water vapor pressure. Bearing this in mind, the salt for calibration has to be prepared with a high precision to minimize the influence from the experimental preparation by precisely weighing the dry salt and the exactly needed added water for reaching equilibrium RH of the solution.

The small size of the calibration sample used in the DVS instrument (~ 25 mg) means that a small moisture change can result in substantial dissolution of the salt. In principle, the concentration of the solution is fixed at the solubility limit of the salt as long as some crystals are present; however, in practice, it is found that the calibration of the RH has an uncertainty as large as $\pm 2.5\%$, if the moisture content of the sample is not properly controlled. Such an uncertainty might be related to the competition between the kinetics of dissolution of the salt, diffusion of ions within the sample, and exchange of moisture with the environment as the RH changes with time. Although the details of the mechanism have not been quantified, the procedure described in this work guarantees a highly accurate and reproducible calibration for single and mixed salts.

The present work aims to describe how a highly accurate calibration of the DVS instrument can be achieved by using the well-defined equilibrium RH of the salt solutions. To avoid unwanted effects during this calibration, it is necessary to take into account the specific properties of each salt, crystal size, reaction kinetics, released heat, and hydration state. Both the basic principle of the DVS instrument and its potential influence on the results are described below. The most accurate calibration method for each considered salt is clarified and discussed.

II. SALT PHASE TRANSITION AND MEASUREMENT

A. Phase transition and crystal size dependence

For pure single salts, the deliquescence point or deliquescence relative humidity (DRH) is the humidity level above which a solid begins to absorb moisture from the surrounding atmosphere.⁴ The deliquescence point for a salt is defined as the onset of dissolution.⁵ For pure single salts, the DRH is identical to the equilibrium RH of the solution. Crystals dissolve completely if the DRH is exceeded. Prior to the deliquescence point, a water film may form, as shown for NaCl.⁵ It is evident that some ions are present within the thin water films resulting in non-accurate transition from salt to solution for NaCl; however, the mechanism of salt dissolution has thus far been poorly described.⁵

The solubility of solids is size-dependent; however, the effect of curvature on the interfacial energy of the crystal–liquid interface is negligible at crystal sizes greater than $0.1\ \mu\text{m}$.⁶ A system can reach thermodynamic equilibrium provided that thermal equilibrium, mechanical equilibrium, and chemical equilibrium coexist.⁷ Because equilibrium between the salt and the ambient air is reached after a relatively long time, in salt–water interactions, the kinetics of phase change must be considered when analyzing salt crystallization.⁸

B. The contribution of the kinetics

To minimize experimentally induced errors, it is beneficial to be able to use as many measurement results as possible and for this purpose, the limiting conditions are examined in the following. The boundary conditions are dependent on the kinetics. In general, adsorption diagrams are plotted as the logarithm of vapor pressure ($\ln P$) against the reciprocal of the temperature ($1/T$), since the lines pictured for the layer of condensation and phase boundaries tend to be straight lines in such diagrams. This is explained by the nearly constant heats of condensation (also called heats of adsorption), as described by the Clausius–Clapeyron equation. The differential heat of adsorption, q_i , is defined by⁹

$$q_i = -k_B \frac{\partial \ln P}{\partial (1/T)} |i\text{-layer}, \quad (1)$$

where k_B is Boltzmann's constant and the i th-layer is the layer for which the differential heat of adsorption is determined. Equation (1) describes a general link between the pressure and adsorption.

A practical way to measure the equilibrium RH for a solution, RH_{eq} , is to take into account the kinetics of dissolution during deliquescence; to this end, an empirical relation to determine the deliquescence point has been deduced.¹⁰ During a phase transition induced by a change in the relative humidity (e.g., a deliquescence reaction carried out at various constant values of RH that lie above RH_{eq}), the total reaction time (t_c) increases with proximity of RH to RH_{eq} . An accurate empirical expression relating the dissolution time to the imposed RH is¹¹

$$\text{RH} = \text{RH}_{\text{eq}} \exp(B t_c^{-1}), \quad (2)$$

where B is an adjustable parameter and can be determined by linear least squares analysis from experimental measurements of t_c at different levels of relative humidity. Equation (2) was shown to be valid for deliquescence of NaCl by using X-ray diffractometry under controlled conditions of temperature and relative humidity (RH-XRD).¹¹

When RH approaches RH_{eq} in Eq. (2), t_c is very large and the curvature of the curve calculated by (2) would then be relatively small. Provided RH approaches RH_{eq} and t_c is very large, the empirical kinetic equation (2) can then be approximately linearized. As clearly illustrated by the result of the calibration test, Figure 3(a), the relation mass-change over time and humidity-difference is also linear in the vicinity of moisture equilibrium such that

$$\frac{dm}{d\text{RH}} = c (\text{RH} - \text{RH}_{\text{eq}}), \quad (3)$$

where dm is the change in sample mass, $d\text{RH}$ is the change in relative humidity, and c is an experimentally determined constant.

Below the deliquescence point, the salt–water mixture is not in equilibrium with the ambient water vapor pressure and hence water evaporates from the solution to reach equilibrium moisture state ($dm/dt < 0$). Conversely, above the deliquescence point, the salt–water mixture accumulates water to reach equilibrium moisture content ($dm/dt > 0$). The equilibrium point is found when $dm/dt = 0$. In principle,

this could be found from the raw data, but the extremum is more reliably identified by using Eq. (3), which is physically reasonable and serves to smooth the experimental data.

C. The influence of the salt state

The activity of water in a salt solution, at equilibrium, equals the relative humidity of the surrounding atmosphere. In an aqueous solution with ideal thermodynamic properties, the mole fraction of water (x_1) is a direct measure of its activity (a_1^{id})

$$a_1^{\text{id}} = x_1. \quad (4)$$

In other words, the standard state, here pure water (l), is the state for which the activity of the component is unity. In the mixture $x_1 < 1$ and hence the activity (a_1)^{id} is also less than unity.¹² Hence, the water activity of a supersaturated solution is always smaller than that of the saturated solution.⁶

D. Released heat

When using salts for calibration of instruments, one has to isolate the desired effect of the salt for the calibration (namely, the dissolution-crystallization equilibrium) while minimizing all other effects (especially the heats of solution and condensation). In general, a spontaneous phase transition from the liquid to the crystalline state can only take place if crystallization lowers the internal energy of the system sufficiently to outweigh the loss in entropy; that is, the transition is “energy driven.”¹³ The enthalpy of solution, ΔH_{soln} , is the heat generated or absorbed when a certain amount of solute dissolves in a certain amount of solvent¹⁴

$$\Delta H_{\text{soln}} = H_{\text{soln}} - H_{\text{components}}. \quad (5)$$

The enthalpy change in an exothermic process (resulting in heat release) is defined as negative. At the equilibrium RH of the saturated solution, three phases are in equilibrium (s, l, g).¹⁵ To reach equilibrium, the amount of heat exchanged required will depend on the type of salt used. If a quantity of liquid condenses into, or evaporates from, a supersaturated solution, the amount of heat exchanged at a constant temperature is given by

$$\Delta H_{\text{condensation}} = H_{\text{liquid}} - H_{\text{vapor}} = -\Delta H_{\text{vap}}. \quad (6)$$

The heat of condensation for a monolayer of water molecules is a measure of the sum of the binding energy of one adatom to the solid.⁹ The heat required depends on the interaction between water and the absorbent.¹² Since heat will affect the temperature of the microclimate surrounding the salt and since the equilibrium moisture state of salts is temperature dependent, the contribution from heat release can affect the accuracy of measurement of the equilibrium moisture content, and therefore, also the calibration of the DVS instrument. The influence of released heat is examined and discussed in Sections V B and V C).

III. GENERAL DESCRIPTION OF THE DYNAMIC VAPOR SORPTION INSTRUMENT

A dynamic vapor sorption (DVS) instrument is used for making continuous mass measurements of a sample in a chamber in which the environmental parameters, including temperature and vapor pressure, are monitored and controlled simultaneously. The balance in the specific equipment used in this study (DVS Advantage 1, Surface Measurement Systems, Alpertown London, United Kingdom) is, according to the manufacturer, able to measure the mass of a sample with a sensitivity of $\pm 0.1 \mu\text{g}$ (if calibrated monthly) for a recommended sample mass between 20 and 30 mg.¹⁶ Using a dew point analyzer (DPA), the vapor pressure in the chamber can be measured within an accuracy of $\pm 0.1\%$ RH.

There is a continuous and constant flow of air (adjustable in the range 100–200 SCCM/min) through the test chamber. The air is a mixture of fully water vapor-saturated air and very dry air with a dew point of at least -80°C . The vapor pressure of the air mixture flowing through the test chamber is controlled by mass flow controllers on the air supplies. There are two ways to control the vapor pressure in the test chamber: by directly controlling the mass flow controllers placed prior to the sample chamber (open-loop control mode) or by including the feedback signal from the DPA, placed just before it enters the sample chamber, to control the mass flow regulators (closed-loop control mode).

A. Open-loop control mode

The amount of moist air supplied is calculated knowing the inner diameter of the air pipe and the air velocity, under the assumption that one of the two air sources is fully saturated and the other is extremely dry. However, the target values do not account for leakage and friction within the system. To compensate for this, salt calibration tests are carried out. When the physical properties of the salts are known, corrections can be made in the instrument's software in a so-called “look-up table”, which is then used to tune the control of the mass flow controllers. The open-loop control mode relies on the fact that leakage and friction are fully accounted for by the look-up table and that it is possible to interpolate between the specific values at which the calibration tests with salts are performed. The advantage of using the open-loop control mode is that changes are controlled to occur continuously. The precision of controlling the vapor pressure when running an open loop is therefore dependent on tabulated values from calibration of the valve controlling the supply of the dry and moist air. It is possible to simultaneously monitor the vapor pressure during an open-loop test with the DPA and thereby obtain two independent values of the vapor pressure.

B. Closed-loop control mode

For a closed-loop calibration, the DPA measures the relative humidity just before it enters the sample chamber and controls the openings of the mass flow controllers through a feedback system. The difference between the measured RH and the target RH is adjusted by changing the mixture between the dry and moist air that flows through the sample chamber.

When using the closed-loop control mode, there is higher fluctuation around the target value compared with that in the open-loop control mode; however, the RH measurements correspond to the RH measured by the DPA at all times.

The precision of a closed-loop calibration is hence dependent on the precision of the DPA. The accuracy of the DPA is dependent on its calibration and adjustment of the offset of the DPA when installed in the DVS. The instrument temperature is adjusted to fit the given dew point temperature at which a liquid droplet film forms on a special optical mirror by changing the offset of the DPA. This dew point temperature is then converted into the solvent (water) partial pressure using the sample temperature and the standard vapor pressure tables for the solvent (water) in question. As a result of a nonlinear relationship between the vapor saturation pressure and the temperature, large deviations can occur with increasing RH.

IV. EXPERIMENTAL

The key to accurate calibration is to add the optimal amount of water to the salt sample, as explained below. The dry salt (analytical grade) was stored in a dry climate desiccator (RH < 5%) until use. Just before use, water was added as small droplets within a climate chamber at a temperature of $20 \pm 1^\circ\text{C}$ to minimize an additional effect from varying temperatures during the salt preparation for the calibration tests with salts. The small water droplets were added until the salt changed from grain to flake consistency ultimately becoming a rounded lump of the salt–water mixture. At the critical equilibrium moisture content (provided a thermodynamical approach for water vapor potential, according to the water activity in the saturated salt solution and given an insignificantly curved liquid–vapor interface), the lump containing the undissolved salt and its surrounding saturated aqueous electrolyte solution takes up or releases water until a free energy minimum is achieved. In particular, the volume of saturated aqueous electrolyte solution containing undissolved grains of salt adjusts to form a lump with a minimum of interfacial area at the liquid/vapor interface. A bigger and rounder spherical shape indicates deliquescence.¹⁷ In the present study, it was observed that the sharp edges of the grains become rounded as the salt grains take up water. This is consistent with previously photographed changes of the state of salts when reaching the equilibrium moisture content.¹⁷ In the present work, an amount of 25 mg dry salt was used for each calibration, which is small enough to provide sufficiently rapid equilibration, but large enough to yield high accuracy.

At the right proportion of salt and water, it is possible to form a salt–solution lump with a glazy but opaque surface. The presence of a lump indicates that there is an excess of water above the deliquescence point. Excess water can also be seen when the salt leaves a trace of water when moved on a surface. The minimal moisture content for reaching equilibrium was determined and this water content (mass %) was used in subsequent preparations of the same salt. The precision for which the equilibrium RH of the salt/water lump can be reached for the salts: LiCl, MgCl₂, Mg(NO₃)₂, NaCl, and KNO₃ is shown in Figure 1.

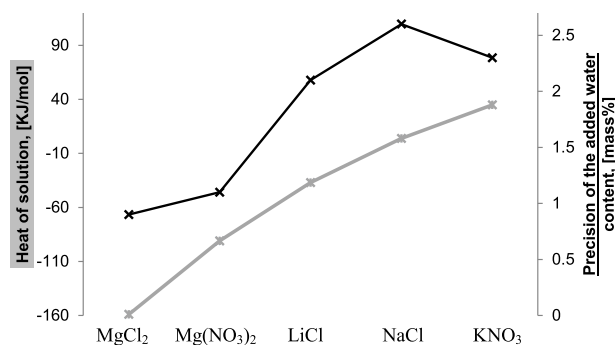


FIG. 1. Precision (x-marker) of reaching equilibrium RH of the solution of the salt/water lump for different salts (right ordinate) related to their heat of solution ordered by decreasing exothermal heat of solution shown on the left ordinate. To prepare the salt–water mixture water was added to the dry salt and, the initially anhydrous MgCl₂ and Mg(NO₃)₂ transformed into the hexahydrates MgCl₂·6H₂O and Mg(NO₃)₂·6H₂O. The results are based on 8–20 preparations for each salt.

The visual method used to determine the optimal salt–water balance was relatively simple, as shown in Figure 2. After the dry salt was prepared to equilibrium RH of the salt/water lump, we could validate the equilibrium RH by using the standard graphs for salt calibration tests, as outlined in Section V A.

V. RESULTS AND DISCUSSION

A. Determination of the equilibrium RH of the solution

The measured masses of the salt solution at the present RH within the sample chamber are accurately described by Eq. (3), as shown in Figure 3. Very similar results were obtained for both the desorption and adsorption phases, as shown in Figure 3(a) (subscript 1 for desorption and subscript 2 for adsorption). To ensure that the salt–water lump reached RH_{eq}, RH > RH_{eq} was established for 1 h; during this time, the mass increase was a result of reaching RH_{eq} throughout the salt–water lump, involving partial dissolution of the salt.

If the salt–water mixture was not in equilibrium (Section IV), the intersection of the two fitted lines (absorption and desorption) would not occur at the point of zero mass change (where $dm/dRH = 0$ in Figure 3(a)). If the salt is too wet, the intersection between the two fitted lines would occur above the y-axis in Figure 3(a); conversely, if the salt is too dry, the intersection would occur below the y-axis.

By ensuring a general linear relationship between the measured mass change and RH change, it is indicated that experimental conditions are satisfactory, ensuring minimum influence from the experimentally induced circumstances (e.g., heat of solution and random deviation). The intersection of the linear relation for dm/dRH at $y = 0$ is used to determine the equilibrium RH of the salt solution, as described in Section II B. This is done to determine both equilibrium RH of the solution during desorption and during adsorption.

The RH within the sample chamber must be changed slowly enough to allow equilibrium between the salt and the surrounding RH to be achieved (Section II B). Adjustments of dRH/dt may therefore be necessary to ensure that the experimental conditions are satisfactory. Under equilibrium

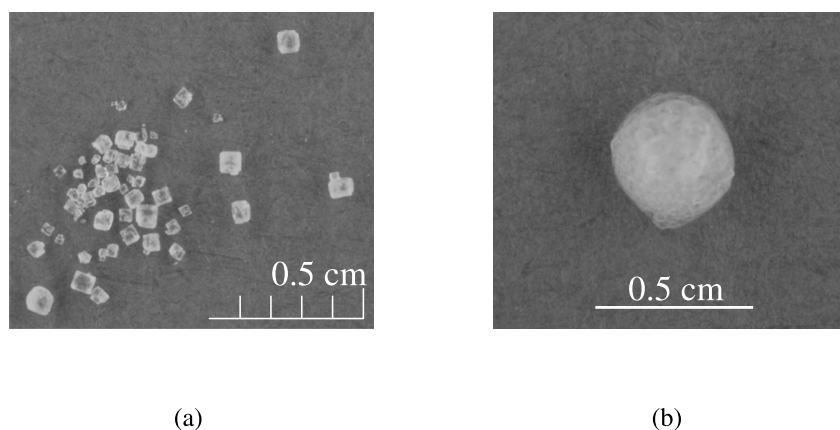


FIG. 2. Images of NaCl: (a) in dry condition and (b) at the equilibrium RH of the solution. The pictures are made with a macro lens, Nikon D 610 (24 Megapixel), Kaiser RB 5000 Daylight Copy Light Set at 5.5 cm between lens and salt.

conditions, the fitted lines for absorption and desorption should coincide at the point of equilibrium; therefore, this can also be used as a measure to determine whether the calibration tests with salts have been carried out under equilibrium conditions. The results can be considered reliable only if: (i) the mass change relative to RH change is linear and an accurate curve fit is possible; (ii) the equilibrium RH of the solution during absorption coincides with that during desorption; and (iii) a continuous mass change occurs. An example of measured and fitted values is shown in Figure 3(a).

B. Conditioning of the solid salt prior to the salt calibration test

The water activity and the corresponding equilibrium RH of the solution are dependent on the concentration of the solution. It has been shown that the equilibrium RH of the solution decreases with increasing molality of the solution, approaching a lower equilibrium RH of the solution at above 10 mol kg⁻¹.⁶ Therefore conditioning of the salt is essential prior to the calibration tests with salts.

Following the procedure described in Section IV, we were able to ensure accurate preparation of the salt prior to salt calibration in the DVS instrument. The precision of reaching equilibrium RH of the salt/water lump (mass of water in relation to the dry salt mass) is shown in Figure 1.

The present results in Figure 1 suggest that there is a link between the heat of solution for each salt and the precision with which the salts can be brought to their equilibrium concentration in water, as salts with higher heat of solution have a more precise transition between the solid and aqueous phase compared with salts having a lower heat of formation. This again will affect the accuracy of the calibration of the DVS instrument, varying for each RH dependent on the salts used at this RH. This was seen in the form of the results for MgCl₂ and Mg(NO₃)₂, salts with a relatively high heat of solution can be prepared with a higher accuracy (with a deviation of 0.9 mass % and 1.1 mass % added distilled water to the dry salt, respectively) than salts with a relatively lower heat of solution, such as LiCl and KNO₃ (with an inaccuracy of 2.1 mass % and 2.3 mass % added water, respectively). A special case is NaCl that compared to the other salts used possesses

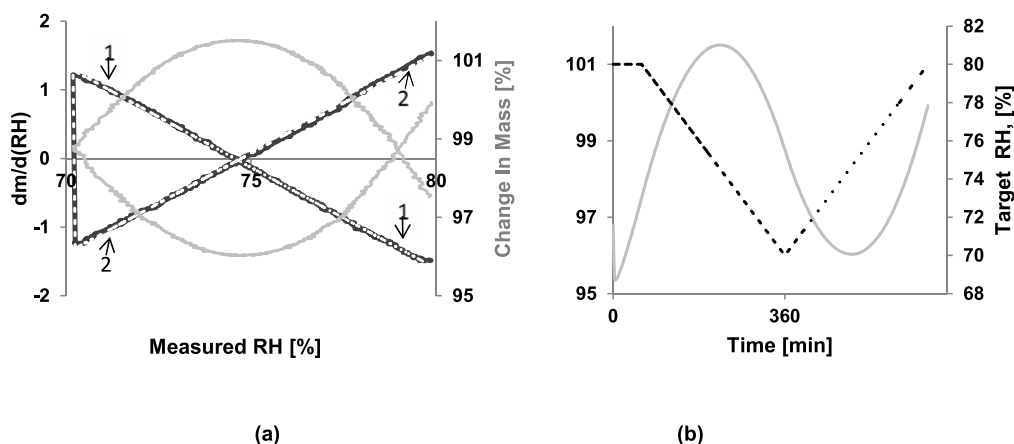


FIG. 3. Plot of the calibration test with the salt NaCl at 25.0 °C. The shown results was obtained with open-loop control mode and a humidity rate change of 2% RH/h. (a) Black line shows the measured $dm/d(RH)$ (within the sample chamber with the DPA), \square fitted $dm/d(RH)$ (calculated with Equation (3)), gray line—change in mass (%) as a function of the actual measured RH within the sample chamber with the DPA. The desorption phase is shown with the subscript “1” and the adsorption phase with the subscript “2” (b) ... is the programmed target RH throughout the calibration test with the salt, gray line is the change in mass (%) as a function of the actual measured RH within the sample chamber with the DPA.

a relatively low heat of solution and an extraordinarily high inaccuracy of 2.6 mass % added water. This is likely caused by the unclear phase transition due to the presence of ions in the thin water film on NaCl prior to the deliquescence point (Section II A).^{4,5} A phase rule for the studied geometry was presented that allows for the coexistence of liquid, solid, and vapor for the binary NaCl–H₂O system across a range of vapor pressures.⁴ This phenomenon is explained by the significant role of the sample–substrate interface as an energy term so that the aqueous and solid phases of NaCl coexist over a perceptible range in their experiments in comparison with observations of free-floating pure NaCl aerosol particles.⁴

C. Development of the most accurate method for determining the equilibrium RH of the solution for a specific salt

1. Specific methods for each salt

As described in Section II, salts have significantly varying properties, requiring individualized methods for each salt calibration test. The calibration with salts is initiated with evaporation until the RH drops below the equilibrium RH of the solution followed by absorption to obtain the most accurate results of the equilibrium RH of the solution.

The required water content to change the salt from a dry salt to its equilibrium RH of the solution is shown in Table I for the five salts studied. The measurements were conducted on a scale with an accuracy of 0.1 mg. The water added during salt–water mixture preparation influences the environment in the sample chamber; each calibration with salts is initiated by evaporation from the salt–water mixture, which produces heat of condensation. In addition, upon reaching the equilibrium RH of the solution, a phase change occurs and results in a contribution from the heat of solution. Although the sample chamber within the DVS is at a constant temperature, such contributions could potentially influence the environment to some degree. We therefore examined these contributions to ensure highly accurate calibrations.

By calculating the moles of each salt (0.025 g dry salt) for the salt calibration and considering the added water and the resulting solubility of each salt, the heat released during partial dissolution was determined to be -5.1 J, -2.6 J, -0.5 J, 0.1 J, and 0.5 J for LiCl, MgCl₂, Mg(NO₃)₂, NaCl, and KNO₃, respectively (Equation (5)). Although different, they were all within the same order of magnitude. The heat of condensation was calculated assuming that all the water added to each dry salt to obtain the equilibrium RH of the solution (see Table I)

had to condense during the calibration tests with the salts (Equation (6)). This added water was then converted to moles of H₂O to calculate the potential heat of condensation. The heat of condensation was calculated to be -17 J, -5 J, -10 J, -12 J, and -11 J for LiCl, MgCl₂, Mg(NO₃)₂, NaCl, and KNO₃, respectively. However, this is a slight overestimation of the contribution from the heat of condensation, since not all of the added water will evaporate during the calibration tests with salts. Depending on the extent of the contribution from the enthalpy of solution, other calibration methods with salts are more suitable. The influence from the enthalpy of solution on the measured result can be minimized by performing calibration tests with salts over the widest possible RH interval within which Equation (3) is valid. However, for salts whose contribution from the enthalpy of solution is dominant in relation to the heat of condensation, it will be more difficult to obtain equilibrium conditions throughout the calibration test. By increasing the duration of the calibration tests with salts, the influence of the enthalpy of solution on the microclimate inside the sample chamber will decrease since there is a constant air flow inside the sample chamber. This will minimize the effect of heat of solution on the equilibrium RH of the solution. This ensures a more representative determination of the phase transition. Narrowing of the RH interval was therefore relevant for LiCl and MgCl₂ to minimize the effect of the heat of solution on the calibration tests with these salts. With regard to KNO₃, we also chose to use a reduced RH interval because the DVS could not perform a calibration starting 5% above the equilibrium RH of the solution, which is 98.58% RH. By narrowing the RH interval around the equilibrium RH of the solution, the highest % RH of the method was 95.08% RH.

A relationship was found between the amount of water added and the duration of continuous absorption or desorption during which Equation (3) is valid (Table I). Such a relationship was fixed in order to obtain reliable results. It was determined that approximately 3% w/w (water mass/solid salt mass) additional water was required for each additional hour the sequence was continued. Table I shows the rate of change in RH per hour and the interval around the equilibrium RH of the solution for the most reliable calibration tests of the DVS instrument.

In a previous work,² only one type of methods was used for all the calibration tests with salts, independent of the specific salt used. In the equipment manual,¹⁶ the use of open-loop control mode is recommended, at an interval of $\pm 5\%$ around the equilibrium RH of the solution and a duration of 10 h for all five salts (LiCl, MgCl₂, Mg(NO₃)₂, NaCl, KNO₃)

TABLE I. Overview of the methods that produced the most reliable results for the salts LiCl, MgCl₂, Mg(NO₃)₂, NaCl, and KNO₃ and water uptake during preparation for the calibration tests with salts.

Salt	Water added during preparation (%)	Duration of test (h)	Adsorbed water per hour of test (%)	Δ RH per hour	Interval around the RH _{eq} (% RH)
LiCl (16 samples)	27.8 ± 2.1	20 (21) ^a	2.8	0.3	± 1.5
MgCl ₂ (20 samples)	8.0 ± 0.9	6 (7) ^a	2.7	1.0	± 1.5
Mg(NO ₃) ₂ (8 samples)	15.8 ± 1.1	10 (11) ^a	3.2	2.0	± 5.0
NaCl (15 samples)	18.7 ± 2.6	10 (11) ^a	3.7	2.0	± 5.0
KNO ₃ (8 samples)	18.2 ± 2.3	20 (21) ^a	1.8	0.3	± 1.5

^aAll the tests started with 1 h at the highest RH (1.5% or 5.0% RH above the reference equilibrium RH of the salt solution).

for the calibration tests with salts. This should achieve an accuracy of $\pm 1.5\%$.¹⁶ Various RH rates (0.5%, 1%, and 2% RH/h) were tested to approach equilibrium conditions during the measurements.¹⁸

2. The influence of the control mode

To study the influence of the two different control modes (open and closed loop), identical calibration tests with salts were carried out with varying RH rates (Figure 4). Figure 4(a) shows the results obtained with the closed-loop control mode. In Figure 4(a), it is evident that the smallest deviations corresponded with the slowest rates of RH change. This is caused by the fact that when using a closed-loop control mode, continuous adjustments are made in relation to the measured RH within the sample chamber. This means that if the phase transition reactions (enthalpy of solution) influence the temperature, and by extension the RH within the sample chamber, the RH is adjusted accordingly. Depending on the rate of change used in the calibration tests with salts, the result will be a more or less continuous change of the mass, thereby influencing the representativeness of the fitted lines. The influence of increased time on the change in RH (dRH/dt) with closed-loop control mode is shown in Figure 4(a) as a function of the increasing enthalpy of solution caused by phase transition. For LiCl and $MgCl_2$, where the contribution from the heat of solution is highest, it is seen that a smaller difference between the obtained values and the reference ones is obtained when the RH interval around the equilibrium RH of the solution is reduced during the calibration tests with salts.

For the other salts, where the least difference between the obtained values and the average reference equilibrium RH of the solution was observed with control mode closed-loop (Figure 4(a)), the measured values of the equilibrium RH of the solution did not differ significantly from the reference values for $Mg(NO_3)_2$, LiCl, and KNO_3 ¹⁹ using the criteria of 1% confidence.²⁰ The equilibrium RH of the solution for

$MgCl_2$ was $33.04\% \pm 0.13\%$ RH, which agrees well with the reference value, $32.78\% \pm 0.16\%$ RH,¹⁹ despite the fact that it had the highest enthalpy of solution during dissolution among the five salts. The equilibrium RH of the solution for NaCl was determined to be $75.62\% \pm 0.37\%$, which is consistent with the reference value, $75.29\% \pm 0.12\%$ RH, despite the unclear phase transition observed for NaCl. By using a cooling stage in an environmental scanning electron microscope (ESEM), it has been shown that there is no clear transition at the deliquescence point for NaCl²¹ as described in Section II A. Random nucleation was observed for NaCl in eight attempts to reach the equilibrium RH of the solution in a NaCl particle at 25 °C.²² Using ESEM, it was shown that the water film contained dissolved Na^+ and Cl^- ions and an outer liquid layer of approximately the same volume as the crystal core for relative humidities up to 3% below the equilibrium RH of the solution was found.⁴ ESEM micrographs also showed that the solid and liquid are simultaneously present in significant amounts from 70% to 75% RH.

The high difference between the obtained values and the reference ones determined in relation to the equilibrium RH of the solution of KNO_3 using a RH rate of 2% RH/h was probably caused by the impossibility of using a method starting at an RH 5% above the expected equilibrium RH of the solution. Even though it should be possible to run experiments with RH up to 98% RH, in practice, it is very difficult to generate calibration tests with salts above 95% RH with the available equipment. By using the new calibration methods with salts described in Section V C 1, the difference between the measured equilibrium RH of the solutions and the reference values was significantly decreased. Differences between the obtained values and the reference ones below or equal to the deviations in the reference were obtained.¹⁹

In general, a higher difference between the obtained values and the reference ones was found with the open-loop control mode (Figure 4(b)) compared with the closed-loop control mode (Figure 4(a)). This is primarily caused by the

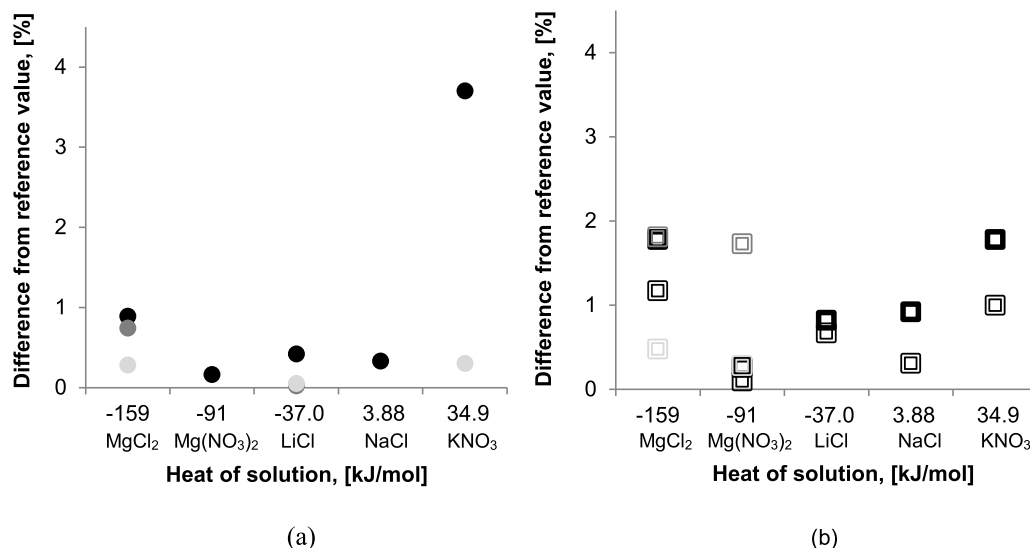


FIG. 4. The results are shown as difference between the obtained values and reference ones¹⁹ for different calibration test methods with salts, where increasing brightness indicates increasing time for the change in RH being: black 2% RH/h, dark gray 1% RH/h, light gray 0.3% RH/h with (a) closed-loop (results shown as circles) and (b) open-loop results (shown as squares) as a function of heat of solution. One calibration series is as a thick line and the other one as double thin lines. All the results are measured with the dew point analyzer (DPA).

dependence of the generated vapor pressure on the water look-up table and the software that controls the supply of dry and moist air according to predefined conditions. The water look-up table is adjusted through calibration tests usually performed during a manufacturer service. These calibration tests with salts are usually carried out within 48 h with related limitations. In Figure 4(b), differences between the measured values and the reference ones with the open-loop control mode are shown in relation to different calibrations and thereby also different water look-up tables. It is evident that the difference between the obtained values and the reference ones was significantly different for those two series apparently performed at identical conditions though differing from the conditions reported in the water look-up tables. However, for all five salts, the difference between the obtained and the reference values was smaller when using the water look-up table that provided the calibration curve with the double thin lines. This confirms the importance of an accurate water look-up table.

In relation to the state of the salt (solid or in solution), the heat of crystallization (Section II C) can potentially affect the actual RH in the sample chamber for a certain period. This means that if the experiments are carried out without ensuring equilibrium conditions, the value obtained will not correspond to the equilibrium RH of the solution. As the generated vapor pressure throughout the sequence in the open-loop control mode only depends on the prior determined sequence related to the mixture of dry and moist air given by the look-up table, this heat release will not be taken into account when using the open-loop control mode. Therefore open loop mode must be used with care.

It is argued that even precise RH sensors cannot measure RH better than the mass flow controllers in the DVS can generate RH.² In practice, these two ways of controlling RH generation are likely to be equally effective, and some manufacturers have incorporated both options in their instruments. However, as shown above, the use of mass flow controllers has some limitations regarding heat release and an accurate water look-up table is essential to generate an accurate pressure within the sample chamber.

Very accurate results were directly measured by the dew point analyzer (DPA) (see Figure 4(a)) during a 2-yr period.

Differences between the obtained values and the reference ones of 0.05%–0.33% RH were found when using the closed-loop mode. However, breakdown of the DPA occurred once or twice a year and each new or repaired DPA had varying accuracy. In previous work, problems were observed with contamination of mirrors in DPA and drift in capacity sensors.² These problems were not observed within the 2-yr period of the present study; the mirror was cleaned before every sequence and drift of the sensor was not observed as similar results were determined at different times, as seen in Section V D.

As the different DPAs had calibrations with varying accuracy, the two control modes (open and closed loop) could be combined to obtain the most accurate results. The combination of the two control modes is made by measuring the RH within the sample chamber with the DPA and generating the vapor pressure with the air flow controllers (open-loop) to account for the accuracy of the DPA calibration (Section V D). This procedure is used in the following.

D. Accuracy and repeatability of the generated pressure

The most reliable calibration tests with salts are outlined in Table I. The calibration tests with salts were carried out as quintuple measurements of the equilibrium RH of the solution for LiCl, MgCl₂, Mg(NO₃)₂, NaCl, and KNO₃ and compared with reference values (see Table II).¹⁹ The deviation in the determination of the equilibrium RH of the solutions of LiCl, MgCl₂, Mg(NO₃)₂, NaCl, and KNO₃ was between 0.06% and 0.15% (0.45% RH for KNO₃) RH. A standard deviation of this magnitude indicates that the determination of the equilibrium RH of the solution was precise. When measuring the RH with the DPA, it is possible to achieve a precision of 0.1% as quoted by the manufacturer. An even higher precision was found with a Dynamic DPA for RH between 50% and 100%, enabling determination of temperature differences with a precision of approximately 0.001 °C.²³

With the present settings of the mass flow controllers (in the water look-up table), the difference between the measured equilibrium RH of the solution of the single salts LiCl, MgCl₂, Mg(NO₃)₂, and NaCl was found to be between +0.17% and –0.77% RH of the reference values.¹⁹

TABLE II. Accuracy and repeatability of the salt calibration tests determined with a generated RH through the air flow controllers (open-loop control mode) and RH measured with the DPA.

Salt	Reference value from the literature	1st run	2nd run	3rd run	4th run	5th run	Average	Difference from the reference value
LiCl	11.30 ± 0.27	11.39 ± 0.05 ^a (12.8.14) ^b	11.50 ± 0.16 (13.8.14)	11.42 ± 0.05 (14.8.14)	11.45 ± 0.11 (10.9.14)	11.60 ± 0.02 (12.9.14)	11.47 ± 0.08	+0.17
MgCl ₂ ·6H ₂ O	32.78 ± 0.16	32.25 ± 0.01 (9.9.14)	32.30 ± 0.04 (3.6.14)	32.25 ± 0.03 (4.6.14)	32.22 ± 0.01 (6.6.14)	32.15 ± 0.01 (8.9.14)	32.23 ± 0.06	–0.55
Mg(NO ₃) ₂ ·6H ₂ O	52.89 ± 0.22	52.21 ± 0.03 (25.3.14)	52.20 ± 0.02 (26.3.14)	52.25 ± 0.11 (27.3.14)	51.90 ± 0.01 (5.9.14)	52.02 ± 0.02 (4.9.14)	52.11 ± 0.15	–0.77
NaCl	75.29 ± 0.12	74.65 ± 0.09	74.58 ± 0.09	74.51 ± 0.17	74.40 ± 0.07	74.69 ± 0.10	74.57 ± 0.12	–0.72
KNO ₃	93.58 ± 0.55	90.93 ± 0.02 (3.7.14)	90.84 ± 0.03 (2.7.14)	90.48 ± 0.22 (9.8.14)	91.55 ± 0.09 (11.9.14)	91.48 ± 0.01 (15.9.14)	91.06 ± 0.45	–2.52

^aThe deviation for each determined equilibrium RH of the salt solution is the difference between the equilibrium RH of the salt solution determined during absorption and desorption.

^bThe date that the measurement was performed is shown in parentheses in the table.

The measured RH of the solution for KNO_3 differs by 2.52 from the equilibrium RH of the solution in the literature.¹⁹ In addition, in the case of KNO_3 , the maximum difference in the determined equilibrium RH of the solution among the results for each of the five different calibration tests with salts was 1% RH. Because the difference between the equilibrium RH of the solution obtained during desorption and absorption within one calibration test with salts was at maximum 0.22% RH, this relatively high difference in the determined RH of the solution is most likely caused by challenges in regards to generating the same RH for all the calibration tests with salts.

Based on the results from Section V C, it is clear that the precision and accuracy obtained by using $dm = 0$ as the equilibrium criterion for the salt–water mixture depends on: the accuracy of the DPA sensor, the step size of the change in RH, and the duration of the calibration tests with salts. The single salts LiCl , MgCl_2 , $\text{Mg}(\text{NO}_3)_2$, NaCl , and KNO_3 have well-defined equilibrium RH of the solutions.¹⁹ The differences between the values measured with the DPA and the reference values should therefore be adjusted. After calculating the differences between the reference values and the measured calibration values for these single salts, the measured equilibrium RH of the solution for the NaCl – Na_2SO_4 and NaCl – NaNO_3 mixtures could be adjusted accordingly and these recalculated equilibrium RHs for NaCl – Na_2SO_4 and NaCl – NaNO_3 mixtures were not significantly different from values reported in the literature,²⁴ suggesting that the computed adjustment was correct.

The equilibrium RH of the solution of charged salt particles individually suspended in an electrodynamic cell by the imposed RH was determined by measuring the abrupt change in the DC voltage caused by changing RH; a reproducibility equal to, or greater than, $\pm 2\%$ was obtained.²⁵ With the DVS instrument, differences of 0.38%–1.1% RH from the literature were found in previous work. The largest difference between the mean of the equilibrium RH of the solutions obtained during absorption and desorption was 0.35% RH for $\text{Mg}(\text{NO}_3)_2$.² For NaCl and $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, it was determined to be $75.4\% \pm 0.5\%$ RH and to $50.8\% \pm 0.7\%$ RH, respectively, using temperature and humidity controlled X-ray diffraction (RH-XRD).¹⁰ Comparison with values obtained from the literature makes it reasonable to characterize the results found in the present study as accurate.

VI. CONCLUSIONS

To obtain the most reliable and accurate results for the equilibrium RH of the salt solutions, it is necessary to create individual salt calibration tests based on the fundamental properties of each salt. Compared with previous works, the method used in this study enables determination of equilibrium RH of the solution with a high accuracy, ensuring finer calibration of the experimental equipment.

For the salt calibration tests, the precision of reaching equilibrium RH of the salt/water lump was found to be essential to obtain accurate results. The equilibrium RH of the solution determined experimentally using the closed-loop control mode in the present work did not differ significantly from the reference values for LiCl , MgCl_2 , $\text{Mg}(\text{NO}_3)_2$, NaCl , and KNO_3 .

Because of the varying accuracy of the DPA, a more robust calibration was obtained by RH using the mass flow controllers (control mode open-loop) and by measuring the RH within the sample chamber (with the DPA) and recalculating the determined equilibrium RH of the solutions relative to the reference values.

The precision of each determined equilibrium RH of the solutions of the salt by the imposed relative humidity of the gas stream was better than 0.5% RH in the present work. In previous works, a precision of 0.5%–0.7% RH was found by using RH-XRD, and salt calibration methods were developed for DVS with differences between 0.38% and 1.1% RH compared with reference values.^{2,10,19} Compared with these results, the present method may be considered more accurate.

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- ¹A. Apelblat and E. Korin, *J. Chem. Thermodyn.* **30**, 59 (1998).
- ²L. Wadsö, A. Anderberg, I. Åslund, and O. Söderman, *Eur. J. Pharm. Biopharm.* **72**, 99 (2009).
- ³I. Rörig-Dalgaard, in *The 3rd International Workshop on Crystallization in Porous Media*, edited by T. Diaz (Portugal, 2012), freely available online through TUE's <http://www.phys.tue.nl/nfcm/cryspom/2012-CryspomIII-abstracts.pdf> and LNEC's websites http://www-ext.lnec.pt/drymass/pdfs/workshop_abstracts.pdf.
- ⁴M. E. Wise, S. T. Martin, L. M. Russell, and P. R. Buseck, *Aerosol Sci. Technol.* **42**, 281 (2008).
- ⁵G. E. Ewing, "H₂O on NaCl: From single molecule, to clusters, to monolayer, to thin film, to deliquescence," in *Structure and Bonding* (Springer-Verlag, Berlin, Heidelberg, 2005), Vol. 116, pp. 1–15.
- ⁶M. Steiger, *J. Cryst. Growth* **282**, 455 (2005).
- ⁷H. P. Freiesleben, in *The Science of Construction Materials*, edited by O. M. Jensen (Springer-Verlag, Berlin, Heidelberg, 2009).
- ⁸R. M. Espinosa and L. Franke, *Constr. Build. Mater.* **22**, 1758 (2008).
- ⁹L. W. Bruch, M. W. Cole, and E. Zaremba, *Physical Adsorption Forces and Phenomena* (Dover Publications, Inc., Mineola, New York, 1997), pp. 249–255.
- ¹⁰K. Linnow and M. Steiger, *Anal. Chim. Acta* **583**, 197 (2007).
- ¹¹K. Linnow, H. Juling, and M. Steiger, *Environ. Geol.* **52**, 317 (2007).
- ¹²F. Toribio, J. P. Bellat, P. H. Nguyen, and M. Dupont, *J. Colloid Interface Sci.* **280**, 315 (2004).
- ¹³D. Frenkel, *J. Phys.: Condens. Matter* **6**, A71 (1994).
- ¹⁴R. Chang, *Chemistry*, 8th ed. (McGraw Hill, 2005), pp. 243–245.
- ¹⁵M. Steiger, *Bauinstandsetzen und Baudenkmalspflege* **11**, 419 (2005).
- ¹⁶Surface Measurement Systems, DVS Advantage Operation Manual, Revision 1.3, n.y., Unit 5, Wharfside Rosemont Road, Alpertown, London HA0 4PE, United Kingdom.
- ¹⁷M. E. Wise, G. Biskos, S. T. Martin, L. M. Russell, and P. R. Buseck, *Aerosol Sci. Technol.* **39**, 849 (2005).
- ¹⁸Q. E. Li and S. J. Schmidt, *J. Food Sci.* **76**, E149 (2011).
- ¹⁹L. Greenspan, *J. Res. Natl. Bur. Stand., Sect. A* **81A**, 89 (1977).
- ²⁰J. N. Miller and J. C. Miller, *Statistics and Chemometrics for Analytical Chemistry*, 5th ed. (Pearson Prentice Hall, 2005), pp. 39–73.
- ²¹I. Rörig-Dalgaard, in *Proceedings from The 4th International Workshop on Crystallization in Porous Media*, The Netherlands 2014.
- ²²C. B. Richardson and T. D. Snyder, *Langmuir* **10**, 2462 (1994).
- ²³O. M. Jensen, *Sens. Actuators A* **181**, 13 (2012).
- ²⁴I. Rörig-Dalgaard, in *Salt Weathering on Buildings and Stone Sculptures*, edited by H. De Clercq (Royal Institute for Cultural Heritage (KIK-IRPA), Belgium, 2014).
- ²⁵I. N. Tang and H. R. Munkelwitz, *J. Atmos. Environ.* **27A**, 467 (1993).